Physical Chemistry Chemical Physics 2018 vol.20 N37, pages 24088-24098

Near-field depolarization of tip-enhanced Raman scattering by single azo-chromophores

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Abstract

© the Owner Societies. The intrinsic symmetry and orientation of single molecules play a crucial role in enhanced optical spectroscopy and nanoscopic imaging. Unlike bulk materials, in which all molecular orientations are unavoidably averaged in the far-field, intensities of vibrational modes in tip-enhanced Raman scattering (TERS) depend greatly on the polarization direction of near-field light. It means that a near-field Raman “dichroism” becomes possible for anisotropic single molecules. Quantitative evaluation of the molecular orientation gets complicated by the depolarization of TERS intensities. Clearly, the depolarization effect is enhanced with an optical antenna and/or a substrate due to their anisotropic origin. In this study, we provide theoretical and experimental insights into Raman tensors of a single azobenzene chromophore, a Disperse Orange 3 (DO3) molecule, supported with a glass base. It is shown that the Raman intensities of the spectral bands corresponding to symmetric and antisymmetric vibrations of the DO3 molecule, for example,-NO2and-NH2moieties, behave differently on the nanoscale. In particular, three-dimensional far- and near-field Raman diagrams indicate that antisymmetric vibrations become highly depolarized, whereas symmetric vibrations remain unchangeable but intensities of their spectral bands are enhanced. Here, we introduce a near-field depolarization factor defined as a normalized discrepancy of longitudinal and transverse TERS signals. We believe that our first steps will ultimately lead to advanced facilities of TERS spectroscopy and nanoscopy, related to the orientation of anisotropic single molecules and their symmetries.

http://dx.doi.org/10.1039/c8cp04887h

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